The effect of annealing on the properties of silicidized molybdenum thin films

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The effect of isothermal and isochronal annealing on the structural and electrical properties of silicidized Mo thin films is reported. The silicidation of Mo with SiH_4 resulted in Mo films with increasing hexagonal $MoSi_2$ content as the reaction time increased. Post-reaction annealing was performed in various ambients (hydrogen, nitrogen, and vacuum) at temperatures from 800 to 1000 °C for times up to 1 h. Annealing in H_2 at 1000 °C for only 5 min results in the virtual disappearance of the original components and the formation of intermediate silicide phases (Mo_5Si_3 and Mo_3Si) and the tetragonal $MoSi_2$ phase. This structural transformation leads to a significant increase in resistivity. The reaction kinetics are considerably slower in the case of N_2 ambient where even after a 60-min anneal at 1000 °C a substantial percentage of Mo remains. This slower rate of phase change is reflected in a more gradual increase in the sheet resistance. The characteristics of vacuum-annealed films followed the N_2 case for short-term anneals ($t \lesssim 10$ min) but resembled the H_2 case longer-term anneals ($t > 15$ min). The dependence of reaction mechanisms on various ambients is discussed.

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I. INTRODUCTION

Refractory metals[1–3] and metal silicides[4–7] are under active investigation as highly conductive interconnect and electrode materials for very-large-scale-integration (VLSI) circuits. One disadvantage of the refractory metals is their poor oxidation resistance. Since their oxides are volatile at high temperatures, surface passivation schemes usually involve deposited dielectrics, as shown in Fig. 1(a). On the other hand, the silicides can generally form a high-quality protective oxide, resulting in a self-passivating structure, as shown in Fig. 1(b). To avoid excessive consumption of the silicide layer during oxidation, a polysilicon pad can be placed[8] between the gate dielectric and the silicide [Fig. 1(c)]. This, however, is at the expense of increased process complexity.

Generally, refractory metal silicide films have been prepared by evaporation or sputtering from either the alloy[4,7] or the individual constituents.[5,6] Recently, it has been shown that $MoSi_2$ films can also be prepared by the reaction of Mo thin films with SiH_4.[9] By this technique, it is hoped that one can combine a refractory metal with an overcoat of its own silicide. The result, shown in Fig. 1(d), is a self-aligned metal-oxide-semiconductor (MOS) electrode structure, the so-called "heart-of-Moly," which has both the high conductivity of the metal and the oxidation resistance of the silicide. The silicidation process resulted in a combination of hexagonal and tetragonal $MoSi_2$, Mo_5Si_3, and Mo_3Si phases. Among the molybdenum silicide phases formed, $MoSi_2$ is the most oxidation resistant and the only silicide phase suitable for self-passivating oxide growth. In addition, in order to realize the advantages of the heart-of-Moly structure, its electrical characteristics must be stable with subsequent high-temperature processing steps. In this paper, we report on the effect of post-reaction annealing conditions (e.g., ambient, temperature, time) on the structural and electrical properties of silicidized molybdenum thin films.

II. EXPERIMENTAL PROCEDURE

The sample preparation and the silicidation process have been previously described.[9] The Mo films used for this study were nominally 3000 Å thick and were silicidized at 800 °C for either 60 or 120 sec. Following silicidation, the samples were annealed under various conditions. Three ambients—hydrogen, nitrogen, and vacuum—were used. For the first two a flow rate of 15 l per min was maintained. In the vacuum anneal cases, a pressure of 2×10^{-7} Torr was used. The anneals performed were either isothermal (1000 °C) or isochronal (5 min). For isothermal anneals, the duration was varied from 5-60 min. For isochronal anneals, the temperature was varied between 800–1000 °C. In all cases, the anneals were not cumulative.

To determine the thickness of the Mo film after silicidation, a step was created in the films by etching in HNO_3/5% NH_4F solution with photoresist masking, and its thickness was measured with a profilometer. The sheet resistance of the films was measured using a four-point probe system. The structural composition was studied using x-ray diffraction performed on a Siemens D500 automatic power diffractometer.

The surface morphology of the films was observed using a scanning electron microscopy (SEM). In Fig. 2, a typical SEM microphotograph of an as-silicidized Mo film is shown. This film was obtained for a 60-sec silicidation at 800 °C. The surface is somewhat rougher than a typical as-

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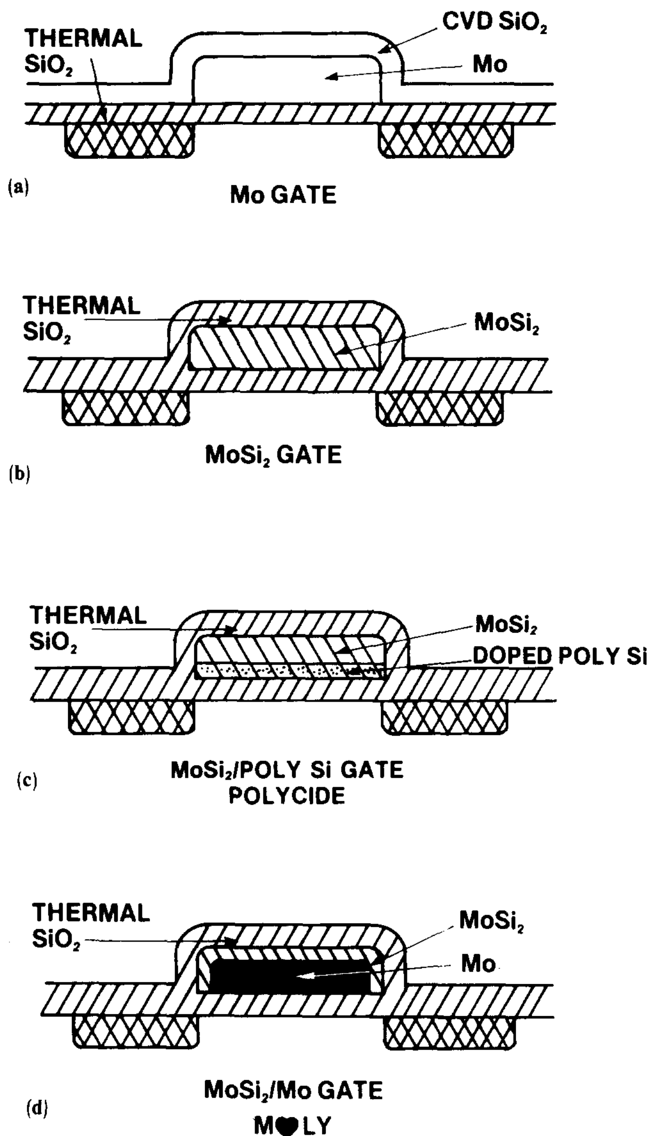

FIG. 1. Schematic cross sections of various refractory gate structures (a) Mo gate, (b) $MoSi_2$ gate, (c) $MoSi_2$/poly-Si (polycide) gate, and (d) $MoSi_2$/Mo ("Heart-of-Moly") gate.

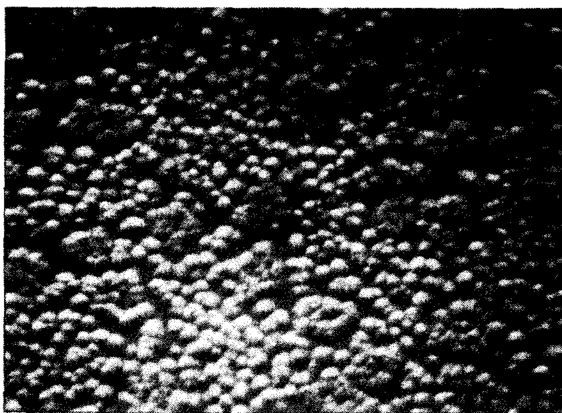

FIG. 2. SEM microphotograph of a typical as-silicidized Mo thin film. Silicidation was done at 800 °C for 60 sec.

sputtered $MoSi_2$ film (picture not shown) obtained by dc magnetron sputtering from a stiochiometric alloy target. The overall adhesion of the silicidized films was good. However, some peeling was observed at the wafer periphery. This stress-induced effect was aggravated for reactions performed at higher SiH_4 flow rates or longer silicidation times.

III. RESULTS

The surface morphology observed after the high-temperature anneals indicated no significant changes. This includes the edge lift-off effect observed after silicidation. Films were reacted at 800 °C with 10% SiH_4 in H_2. The 10% SiH_4 and main H_2 flow rates were 244 cc/min and 30 1/min, respectively. For a 60-sec reaction, the composition of the unannealed films, shown in Fig. 3(a), consists of mainly Mo oriented in the (110) direction.[10] A small hexagonal[11] $MoSi_2$ component oriented in the (111) direction is also observed. This latter component becomes comparable to the Mo peak for a 120-sec reaction [Fig. 7(a)]. In either case, no other silicide phase was observed within the detection limit of the diffractometer.

The structural composition of films isothermally annealed in H_2 at 1000 °C is shown in Figs. 3(b) and (c). As can be seen, even a 5-min anneal in this case results in a drastic change in constituent phases. The Mo component is totally absent, while intermediate silicide phases [Mo_5Si_3 (Ref. 12) and Mo_3Si (Ref. 13)] are now dominant. No further structural change was observed for anneals up to 60 min.

Isothermal annealing in a N_2 ambient at the same temperature (Fig. 4) results in a more gradual Mo to silicide transformation. In this case, the Mo component still dominates after a 20-min anneal and remains significant after 60

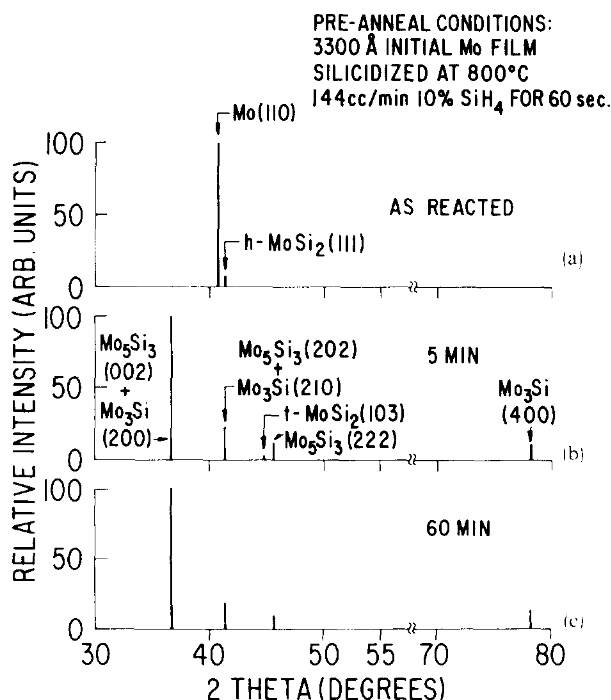

FIG. 3. Relative x-ray intensities (peak values, not corrected for background and normalized to the highest peak) of a 3300-Å-thick Mo film which was first silicidized for 60 sec at 800 °C and then isothermally annealed in H_2 at 1000 °C for (a) 0 min (as-reacted), (b) 5 min, and (c) 60 min.

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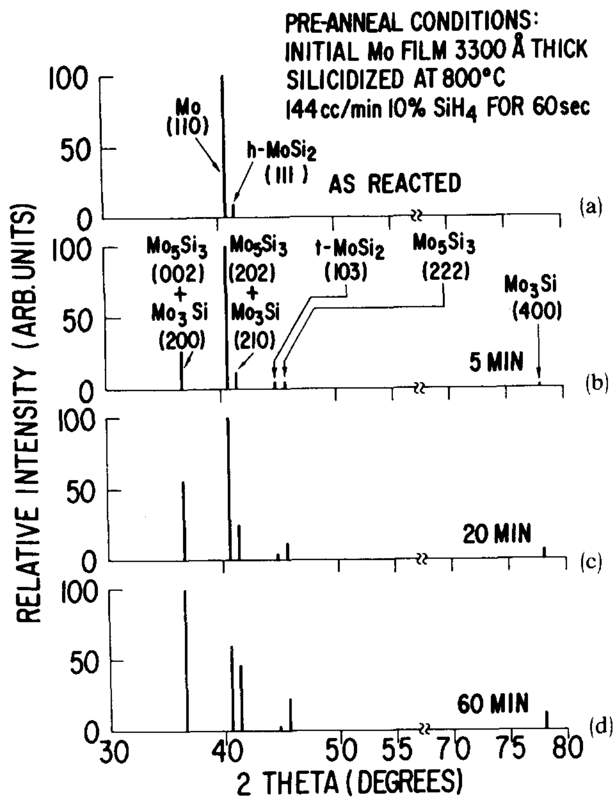

FIG. 4. Same as Fig. 3, except the film was isothermally annealed in N_2 at 1000 °C for (a) 0 min (as-reacted), (b) 5 min, (c) 20 min, and (d) 60 min.

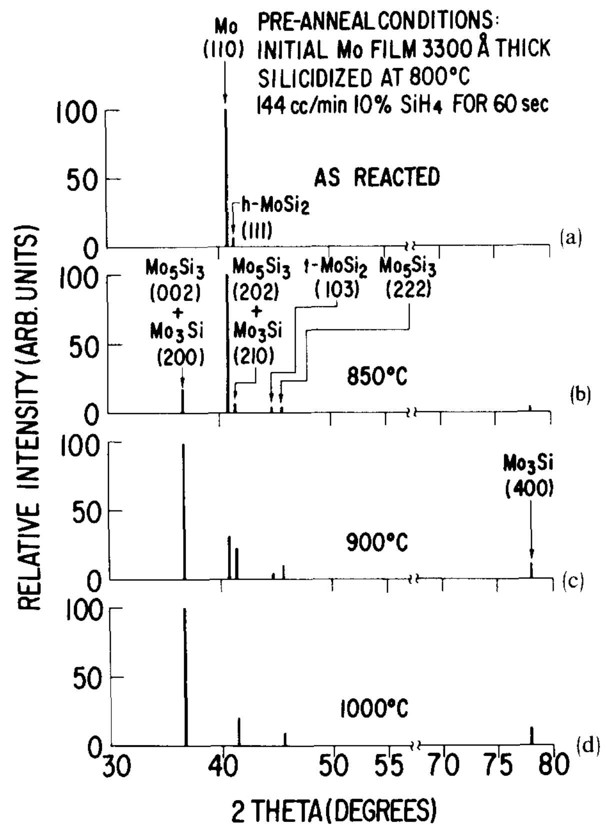

FIG. 6. Relative x-ray intensities of a 3300-Å-thick Mo film which was first silicidized for 60 sec at 800 °C and then isochronally annealed in H_2 for 5 min at (a) 20 °C (as-reacted), (b) 850 °C, (c) 900 °C, and (d) 1000 °C.

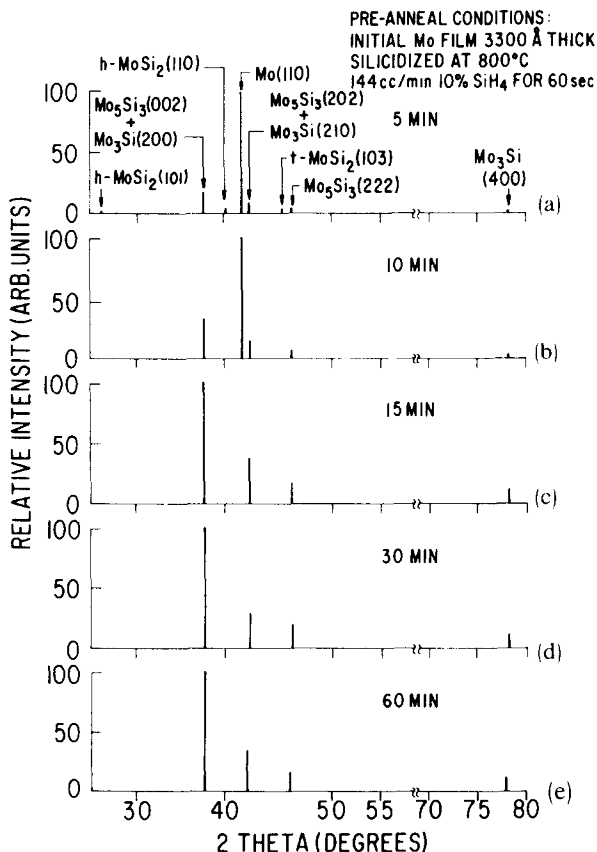

FIG. 5. Same as Fig. 3, except the film was isothermally annealed in vacuum at 1000 °C for (a) 5 min, (b) 10 min, (c) 15 min, (d) 30 min, and (e) 60 min.

min.

The effect of annealing in vacuum (Fig. 5) results in a structural change process which is between those observed in the H_2 and N_2 cases. For a 5-min anneal, the relative peak intensity of Mo to silicides is nearly identical to the N_2 case. On the other hand, after 60 min, the phase composition is very close to that obtained in the equivalent H_2 case, resulting in the complete absence of Mo. While the H_2 ambient the Mo disappears after less than 5 min, this transformation occurs between 10 and 15 min in the vacuum case. In contrast, in the N_2 case, this complete transformation was not observed for anneals up to 60 min.

To further examine this Mo to silicide transformation, isochronal anneals were performed. To accelerate the transformation rate, H_2 ambient was used, thus allowing for a 5-min anneal time. The results of isochronal anneals of a film silicidized for 60 sec are shown in Fig. 6. For an 850 °C anneal, the (110) Mo peak is still dominant. It is interesting to point out that the relative ratio of various phases are similar to those observed for anneals of the same duration in N_2 and vacuum, but at the higher temperature of 1000 °C. Increasing the temperature of isochronal anneal by only 50 to 900 °C results in making the intermediate silicides the dominant phases at the expense of the Mo component.

To evaluate the effect of a larger initial percentage of $MoSi_2$ on the structural transformation, a film silicidized for 120 sec was also subjected to isochronal anneals. In Fig. 7(a), the as-reacted film is shown to be composed of approximate-

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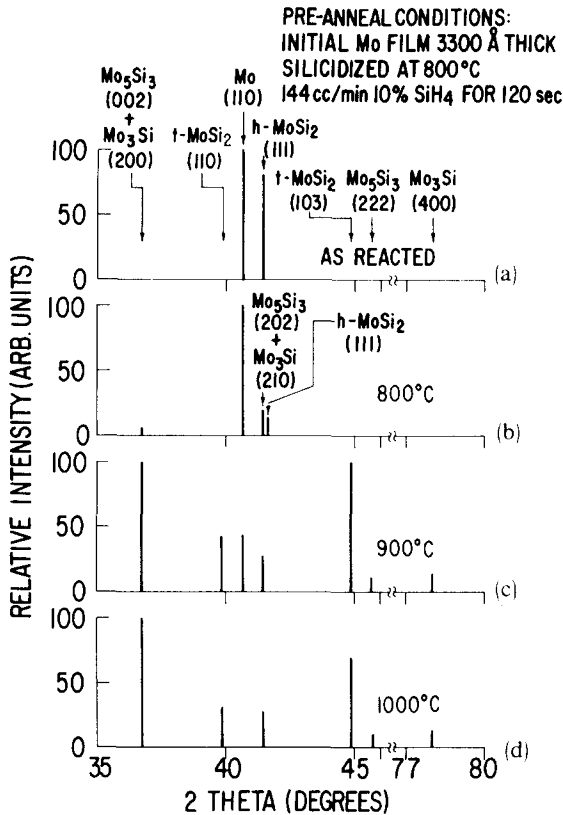


FIG. 7. Same as Fig. 6, except the film was first silicidized for 120 sec and then isochronally annealed in H_2 for 5 min. at (a) 20 °C (as-reacted), (b) 800 °C, (c) 900 °C, and (d) 1000 °C.

ly equal amounts of Mo and hexagonal $MoSi_2$. For a subsequent anneal at 800 °C [Fig. 7(b)], it is observed that the hexagonal $MoSi_2$ phase is greatly diminished while the Mo component is still dominant. Intermediate silicide phases are now also detected. Following an anneal at 900 °C [Fig. 7(c)], the Mo component is seen to be greatly reduced. In its place, large amounts of both intermediate silicides and tetragonal $MoSi_2$ are present. By comparison, the composition of a film silicidized for only 60 sec and annealed under the same conditions [Fig. 6(c)] shows no significant amount of tetragonal $MoSi_2$. Further increase in anneal temperature to 1000 °C [Fig. 7(d)] essentially eliminates the Mo peak and results in a slight reduction in the t-$MoSi_2$ peaks.

While our results were obtained for silicidized Mo thin films it is also interesting to point out that the same transformation has been observed in the bulk.[14] Thick films ($> 40 \mu m$) of $MoSi_2$ grown on bulk Mo are transformed into Mo_5Si_3 and Mo_3Si upon high-temperature (1200–1900 °C) annealing.

Furthermore, from data on heat of formation of various silicides, the change in enthalpy for the change in the reaction of $MoSi_2/Mo$ to Mo_5Si_3 or to Mo_3Si is calculated to be -26 or -29 Kcal/g mole of intermediate silicide formed. To a first approximation, this indicates that Mo_5Si_3 and Mo_3Si have an approximately equal probability of formation.

Turning now to the electrical properties, the sheet resistance (R_s) of silicidized films isothermally annealed at 1000 °C is shown in Fig. 8. The data in Fig. 8 were taken on

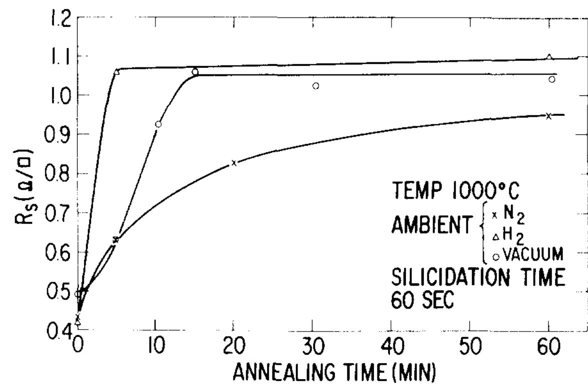
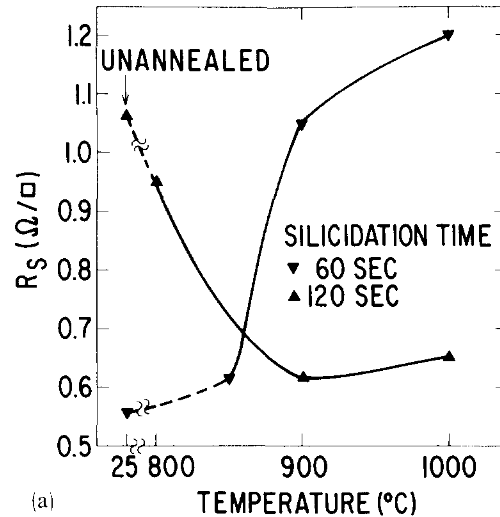


FIG. 8. Sheet resistance of silicidized Mo films as a function of post-silicidation annealing time in various ambients (H_2, N_2, and vacuum) at 1000 °C.

films silicidized for 60 sec. The film thickness measured was 7000-8000 Å. The as-reacted R_s is between 0.4-0.5 $\Omega/\square$. For H_2 anneals, R_s increased rapidly after only a 5-min anneal to a value greater than 1 $\Omega/\square$. Longer term H_2 anneals, up to 60 min, do not significantly affect R_s. On the other hand,



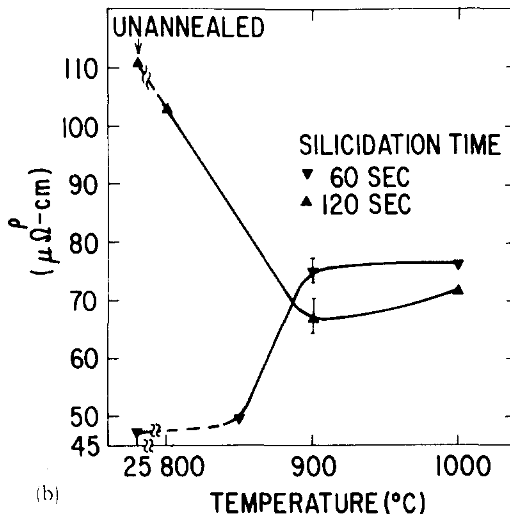


FIG. 9. Isochronal anneal in H_2 for 5 min. (a) Sheet resistance and (b) resistivity of silicidized Mo films as a function of isochronal annealing temperature at silicidation times of 60 and 120 sec.

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anneals in N_2 result in a more gradual increase in R_s with anneal time. After the 5-min anneal, R_s increased by $\sim 50\%$ to $0.62\,\Omega/\square$. After the 60-min anneal, R_s reaches $0.95\,\Omega/\square$ approaching the value obtained in the H_2 case. In the vacuum anneal case, the initial increase of R_s resembles that of N_2, to $\sim 0.65\,\Omega/\square$ after 5 min. Longer term annealing, R_s quickly increases to $> 1\,\Omega/\square$ after 15 min and no significant change was observed up to 60 min. The R_s values obtained for $t_{anneal} > 15$ min are very close to those obtained in the H_2 anneal case.

The dependence of sheet resistance and resistivity on isochronal anneal temperature is shown in Figs. 9(a) and (b), respectively, for films silicidized for 60 and 120 sec. The anneal conditions were 5 min in a H_2 ambient. While the films were 7000-8000 Å thick after 60-sec silicidation, those silicidized for 120 sec had a thickness of 1–1.1 μ. The as-reacted films had an R_s of $0.45\,\Omega/\square$ and $1.6\,\Omega/\square$ for the 60- and 120-sec silicidation, respectively. Annealing the film reacted for 60 sec at temperatures up to 900 °C increases R_s to $1.05\,\Omega/\square$. Anneals at 1000 °C results in only marginally higher R_s. The films reacted for 120 sec exhibit a different dependence. For anneals up to 900 °C, R_s decreases down to $0.62\,\Omega/\square$. Higher-temperature anneals result in a slight increase in R_s.

IV. DISCUSSION

Before correlating the structural and electrical data, it is instructive to consider the resistivity of the various molybdenum silicides, as shown in Fig. 10. In bulk form, three silicide phases have been identified[15]: $MoSi_2$, Mo_5Si_3, and Mo_3Si. The Mo_5Si_3 phase has the higher bulk resistivity, $\sim 50\,\mu\Omega$ cm, while the other two are in the 20-25 $\mu\Omega$ cm range. By comparison, the bulk resistivity of Mo is ~ 5 $\mu\Omega$ cm. In annealed thin films the resistivity is generally higher due to reduced carrier mobility. For example, in the case of $MoSi_2$, the thin film values are between 2 to 4 times higher than the bulk value.[4,16] While actual resistivity values of various silicides depend on the deposition method, the

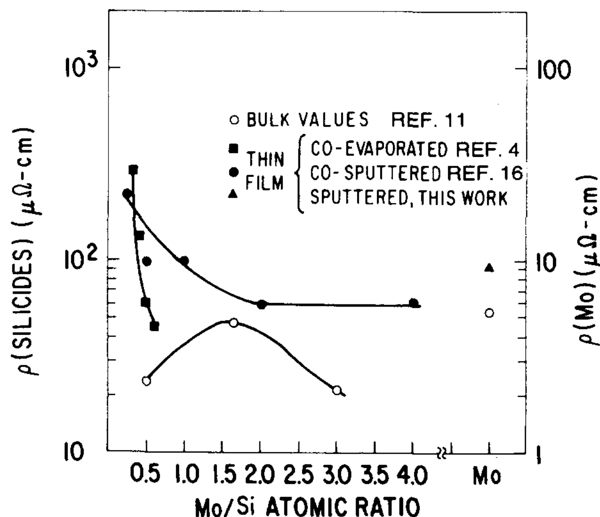

FIG. 10. Bulk and thin-film resistivities of Mo and its various silicides of different Mo/Si ratio.

general trend is one of decreasing resistivity with increasing Mo content. In the extreme, for the sputtered Mo thin films, a resistivity of ~ 8–$10\,\mu\Omega$ cm was measured.

As-sputtered 3300-Å-thick Mo films had an R_s of $\sim 0.35\,\Omega/\square$ prior to the actual silicidation reaction. The Mo films undergo high temperature *in situ* cleaning[9] (1000 °C, 5 min in H_2) which results in a decrease in R_s to $0.25\,\Omega/\square$. Following silicidation for 60 sec, R_s increases to ~ 0.45 $\Omega/\square$. This increase is attributed to the formation of a small amount of $MoSi_2$ [see Fig. 4(a)] which has a higher resistivity than Mo. This process is enhanced when the silicidation time is increased to 120 sec. In this case, R_s is approximately 1.6 $\Omega/\square$ and a substantial amount of $MoSi_2$ is detected [see Fig. 7(a)].

Let us consider first isothermal annealing. In the H_2 case, the rapid formation of intermediate silicides [Fig. 4(b)] is the cause of the sharp increase in resistivity within the first 5 min of anneal (Fig. 9). Longer term anneals result in no further structural change [Fig. 4(c)] and this is reflected in a constant sheet resistance. The more gradual effect of N_2 anneals is seen in both a slower structural transformation (Fig. 4) and a slower increase in R_s. After a 5-min N_2 anneal, the film-still consists mainly of Mo, unlike the H_2 case where Mo_5Si_3 and Mo_3Si dominate. This is consistent with a much lower R_s measured in the N_2 case. After the 60-min anneal, the transformation is still not complete [Fig. 4(d)] with substantial Mo still present. This is reflected in the R_s data which show that saturation is not reached. Vacuum annealing results in characteristics which initially resemble the N_2 case in both structure and resistivity. For 5-min anneals, the R_s obtained in the two cases is the same, with an almost identical structural composition [Figs. 4(b) and 5(b)]. Longer term anneals (> 15 min) result in characteristics similar to those obtained in the H_2 case. In both cases, R_s remains constant with anneal time and no structural change is observed, with the intermediate silicide phases dominating.

Isochronal annealing also results in correlated changes in structural composition and electrical resistivity. Initially, the shorter (60 sec) silicidation time results in smaller amounts of h-$MoSi_2$ formed [compare Fig. 6(a) with Fig. 7(a)] and hence smaller increase in sheet resistance or resistivity [Figs. 9(a) and (b)] than the longer (120 sec) silicidation time. Also, the increase in film thickness is less for the former than for the latter (from 3300 to 8600 Å and 1.05 μ, respectively).

As the postsilicidation annealing proceeds, various silicide phases become the resistivity-determining components, instead of Mo in the as-reacted films. This leads to the different dependence on isochronal annealing temperature for the two silicidation times. Firstly, for the silicidation time of 60 sec, the rapid increase in sheet resistance or resistivity [Figs. 9(a) and (b)] between 850 and 900 °C is due to the structural transformation in which the intermediate silicides replace Mo and $MoSi_2$ as dominant components [Figs. 6(b) and (c)] and thus increase the overall resistivity. Anneals performed at higher temperatures (900–1000 °C) result in little change in either resistivity or structural composition. On the other hand, for the silicidation time of 120 sec, a decrease of R_s or ρ_s is observed between 800 and 900 °C [Figs. 9(a) and (b)],

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together with a significant increase in various silicides [Fig. 7(c)], including t-$MoSi_2$ that compensates for the loss of Mo and consequently lowers the overall resistivity. Also, annealing between 900 and 1000 °C does not affect the resistivity but eliminates all and not some of the Mo. Furthermore, it may be noted that for the two silicidation times, there is a large difference in sheet resistance (1.1 Ω/□ vs 0.65 Ω/□ reached after annealing at the highest temperature (1000 °C, as shown in Fig. 9(a), but that is mostly due to the difference in film thickness, as verified in Fig. 9(b), where the difference, in terms of sheet resistivity, is only 10 μΩ cm.

In general, H_2 appears to act as a catalytic agent during the annealing process, resulting in the rapid transformation of Mo into the silicide phases. This fast reaction rate is probably indicative of grain boundary diffusion of Si. It has been shown[17] that in the Mo/Si thin film interaction, Si is the main diffusing species. Because of the reducing nature of H_2, any trace of oxygen in the ambient is removed, thus preventing any Mo/O_2 or Si/O_2 interaction. In addition, the H_2 also can break up any Mo-O (though not Si-O bonds) within the film, thus further increasing the rate of Mo/Si interaction. On the other hand, the N_2 ambient can be easily contaminated with traces of oxygen, which, by tying up Si or Mo atoms, would slow down the reaction rate. The vacuum anneal removes the possibility of this additional Si/O_2 and Mo/O_2 interactions, but does not eliminate those Mo-O or Si-O bonds already formed. In this respect, one can see how the transformation rate in vacuum falls in between those of H_2 and N_2 ambients. Clearly, more work needs to be done to elucidate the exact mechanisms responsible for the Mo to silicide transformation.

The silicidation reaction has also been attempted with other refractory metals: Nb and Ti. However, we were unsuccessful due to the fact that both Nb and Ti react with the underlying SiO_2 at the high temperature (1000 °C) used for the *in situ* cleaning prior to silicidation. This is consistent with free energy calculations which indicate that in the case of Nb, Ti, and Ta the metal/SiO_2 reaction is favored, while in the case of Mo and W no reaction is expected.

V. CONCLUSIONS

The effect of annealing on the structural and electrical properties of silicidized Mo thin films has been studied. The as-reacted films have Mo and h-$MoSi_2$ as the dominant phases. Upon annealing they are replaced by the intermediate silicide phases, such as Mo_5Si_3 and Mo_3Si, and t-$MoSi_2$. The kinetics of this structural transformation is strongly dependent on annealing ambient and temperature. Among the three ambients (H_2, N_2, and vacuum) investigated, the reaction proceeds fastest in H_2 and slowest in N_2, whereas in vacuum, it initially resembles that in N_2 but follows that in H_2 case for longer-time annealing. A significant increase in resistivity was observed with this structural transformation and has been correlated well with the dissolution on formation of Mo and its various silicides.

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